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# Dechlorination of Trichloroacetic Acid by Mn(III)/oxalate System and the Enzymatic System of Manganese Peroxidase/Mn(II)/oxalate\*<sup>1</sup>

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## Introduction

The accumulation of recalcitrant halocarbonated compounds in soil has caused serious environmental pollutions. However, a variety of environmental pollutants, such as chlorophenol, benzopyrene, and dioxins, have been reported to be degraded by white-rot fungi including *Phanerochaete chrysosporium*<sup>1)</sup>.

The active oxygen species generated in lignin biodegradation system have been considered to be promising for dehalogenation of halogenated compounds. For example, Aust *et al.*<sup>2)</sup> reported dehalogenation of CCl<sub>4</sub> by CO<sub>2</sub><sup>•-</sup> derived from oxalate in lignin peroxidase (LiP)/veratryl alcohol/oxalate system. We report here the enzyme-mimetic dechlorination of trichloroacetic acid (TCA) by Mn(III)/oxalate system and manganese peroxidase (MnP)/Mn(II)/oxalate system for the first time.

## Materials and Methods

The reaction mixture contained 66.7 mM oxalate (pH 5.0), 10 mM Mn(III) acetate, and 33.3 mM TCA was incubated at 30°C. Similarly, 33.3 mM TCA was incubated with 66.7 mM oxalate (pH 5.0), 10 mM MnSO<sub>4</sub>, 6.3 mU of MnP, and 0.3 mM H<sub>2</sub>O<sub>2</sub> at 30°C. After oxalate was removed with Ca(NO<sub>3</sub>)<sub>2</sub> by centrifugation, the amount of Cl<sup>-</sup> derived from TCA was determined spectrophotometrically<sup>3)</sup>.

## Results and Discussion

TCA was found to be nonenzymatically dechlorinated by Mn(III)/oxalate system. The yield reached the maximum (3.2%) by 80 minutes (Fig. 1). Both oxalate and Mn(III) were required for the dechlorination of TCA.

The optimum concentration of Mn(III) in the reaction mixture was 6 mM and the yield decreased as Mn(III) concentration increased. The yield of Cl<sup>-</sup> derived from TCA under anaerobic condition was 5 times higher than that of under the aerobic condition. A proposed mechanism for the dechlorination is shown in Fig. 2. As

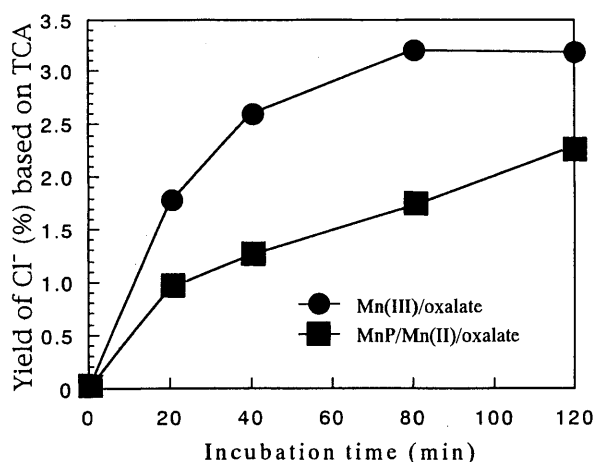


Fig. 1. Enzymatic (MnP/Mn(II)/oxalate) and bio-mimetic (Mn(III)/oxalate) dechlorination of trichloroacetic acid (TCA).

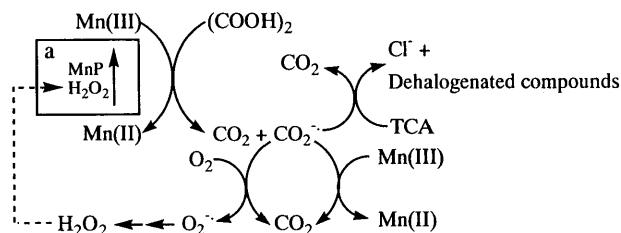


Fig. 2. A proposed mechanism for the dechlorination of TCA by MnP/Mn(II)/oxalate system. note: a, Mn(II) is oxidized to Mn(III) in the enzymatic reaction.

shown by Aust *et al.*<sup>4)</sup>, the reducing active species, such as CO<sub>2</sub><sup>•-</sup> derived from oxalate, were probably responsible for dechlorination of TCA. Because the yield of dechlorination was greater when the reaction mixture showed higher reducing activity of nitrobluetetrazolium (Data not shown), although the author did not confirm the production of CO<sub>2</sub><sup>•-</sup> by ESR. On the other hand, another reducing agent such as O<sub>2</sub><sup>•-</sup> might also be produced during the reaction. However, in separate investigation, TCA was not dechlorinated by O<sub>2</sub><sup>•-</sup> derived from K<sub>2</sub>O (Data not shown), which also supports that CO<sub>2</sub><sup>•-</sup> was an active species for dechlorination.

Similarly, TCA was enzymatically dechlorinated by

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MnP/Mn(II)/oxalate system (Fig. 1). However, Mn(III) was expected to be regenerated by MnP in the presence of  $\text{H}_2\text{O}_2$ . Interestingly, in contrast to the Mn(III) oxalate system, dechlorination reaction occurred in 86% yield based on TCA dechlorinated of the complete reaction system, even though  $\text{H}_2\text{O}_2$  was not added exogenously, suggesting that  $\text{H}_2\text{O}_2$  was produced from  $\text{O}_2$  by the reduction with  $\text{CO}_2^{\cdot -}$  (Fig. 2). Thus, more  $\text{Cl}^-$  would be released in enzyme system than in its biomimetic system during longer periods of the reaction. A possible mechanism for the enzymatic dechlorination of TCA is essentially the same as the non-enzymatic one for the

Mn(III)/oxalate system.

Further research is needed to detect active reaction species such as  $\text{CO}_2^{\cdot -}$  by ESR.

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